Fluorite Precipitation in a Calcareous Soil Irrigated with High Fluoride Water[1]

P. W. TRACY, C. W. ROBBINS, AND G. C. LEWIS[2]

ABSTRACT

Lysimeters filled with Freedom silt loam soil (fine-silty, mixed, mesic, Xerollic Calciorthids) were irrigated with geothermal well water from south central Idaho. The water contained 7 mg F/L. Alfalfa (*Medicago sativa* L.) was grown in the lysimeters and the water was applied at a rate to give either a 0.30 or 0.15 leaching fraction. After irrigating the 1.0 m deep soil samples for 600 d, over 98% of the added F remained in the soil. Soil extract and lysimeter leachate analysis showed that fluorite precipitation was occurring in the upper profile, but only after another fluoride adsorption mechanism was saturated and the fluoride and calcium ion activities exceeded the CaF_2 ion activity product. The F concentration in the upper profile extracts exceeded 20 mg F/L and with the additional high F water irrigation, the soluble F would be expected to leach deeper in the soil. Under field conditions the F would be expected to eventually move into the groundwater with continued irrigation with high F water.

Additional Index Words: ground water contamination, water pollution, fluoride adsorption, leaching, water soluble fluoride.

MOST geothermal spring and well waters being developed for irrigation, space heating, or energy production in the western United States contain high fluoride (F) concentrations (Kubota et al., 1982; Nordstrom and Jenne, 1977). Much of this water will be applied directly to, or disposed of, on calcareous soils. Considerable information is available on F reactions in acid soil and clay systems (Omueti and Jones, 1977) but only limited information is available for calcareous and sodic soils. Brewer (1966) considered total soil F data to be of only academic interest and considered water-soluble F measurements as the best method of predicting F uptake by plants. Likewise, ground water contamination from long-term irrigation with high F water can be expected to be associated with soluble F movement with the drainage water. The maximum legal allowable F concentration in drinking water varies from 1.4 to 2.4 mg F/L, depending on the average maximum daily temperature (Rubel and Woosley, 1978).

Bower and Hatcher (1967) measured F adsorption by eight minerals and six soils which had received different pretreatments and had pH values of from 4.1 to 8.7. They concluded that alkaline soils were limited in their F adsorbing capacity. Gupta et al. (1982) showed that F adsorption was affected by pH but SAR or ESP differences had very little effect on adsorption. Neither of these studies considered adsorption mechanisms in alkaline soils.

Fluorite will readily precipitate from moderately supersaturated solution (Roberson and Schoen, 1973) and since calcareous soils in the 7 to 8.5 pH range contain a continuous soluble Ca supply, fluorite precipitation would be expected when calcareous soils are irrigated with high F water. The purpose of this study was to determine if fluorite precipitation would occur in a saline sodic soil irrigated with a high F geothermal well water.

MATERIALS AND METHODS

Freedom silt loam (fine-silty, mixed, mesic, Xerollic Calciorthids) soil was used in this lysimeter study. This is the predominant soil in a potential geothermal power plant waste water irrigation disposal site in south central Idaho. The surface 0.15 m is sodic and below 0.15 m, the soil is saline sodic (Table 1) and is quite uniform in texture down to at least 5 m.

The lower 0.3 to 1.0 m of soil in each lysimeter was taken from 0.15- to 0.50-m depth of Freedom silt loam and the surface 0.3 m in the lysimeter was taken from the surface 0.15 m in the field. The continuously weighing lysimeter had 10^{-1} MPa ceramic sampling cups at 0.25, 0.50, and 0.75 m and a drain tube and sampling port at the bottom (Robbins and Willardson, 1980). As the lysimeters were filled they were vibrated until the soil bulk density was increased to 1.35 gm cm^{-3}. Alfalfa was planted in each lysimeter for water extraction to concentrate the soil solution. Three lysimeters were irrigated at 0.30 leaching fraction and three were irri-

Table 1—Lysimeter soil and irrigation water chemical composition.

	pH	EC	Ca	Mg	Na	K	SO₄	Cl	HCO₃	CO₃	F
		dS m⁻¹				mmol L⁻¹					mg L⁻¹
Freedom soil 2:1 soil/water											
0 –0.3 m	8.5	2.3	0.5	0.1	23.0	1.1	1.9	13.5	5.0	1.0	0.6
0.3–1.0 m	9.3	16.0	0.4	0.1	163	3.0	11.0	134.0	7.7	1.4	0.8
Water	7.3	2.7	1.6	0.1	23.2	1.0	0.9	24.1	1.4	0.0	7.2

Table 2—Lysimeter water and fluoride balance.†

Lysimeter	Unit	0.30 leaching fraction			0.15 leaching fraction		
		A	B	C	A	B	C
Water applied	L	875	963	378	640	560	236
	mm	1200	1320	518	630	767	323
Leachate	L	259	292	113	96	85	35
	mm	355	400	155	132	116	48
Evapotranspiration	L	616	671	265	544	475	201
	mm	844	920	363	745	650	275
Total F added	g	6.35	6.99	2.74	5.04	4.07	1.72
Leachate F	g	0.13	0.13	0.06	0.04	0.03	0.02
Soluble F	g	1.36	1.45	0.36	0.58	0.51	0.21
Unmeasured F	g	4.86	5.41	2.32	4.42	3.53	1.49

† One pore volume is equal to 37 L or 51 mm of water.

gated at 0.15 leaching fraction with geothermal water from the U.S. Dep. of Energy Geothermal Power Plant in south central Idaho (Table 1). One lysimeter from each leaching fraction was irrigated for 330 d and two lysimeters from each leaching fraction were irrigated for 600 d prior to being sampled at 0.1-m depth increments. The depth of water applied, leached, and used by the growing crop were recorded (Table 2). The fluoride mass balance was also calculated from the F concentrations and water volumes. The lysimeters were in a greenhouse and five alfalfa crops were cut from the 330-d lysimeters and eleven crops were cut from the 600-d lysimeters at 1/10 to 1/3 bloom.

Soil samples from the waste water disposal site, subsamples from the bulk samples used in the lysimeter, and the samples taken from the lysimeters at the end of the study were extracted in 2:1 soil/water ratios for 24 h. These extracts, the irrigation water from the geothermal wells, and the drainage water from the lysimeter drains and ceramic cup systems were analyzed for F ion concentration with an Orion F ion specific electrode. The water samples and extracts were diluted 1:1 with Orions T1SAB[3] buffer solution which acts as an ionic strength and fluoride ion complex buffer. Calcium and magnesium concentrations were measured by atomic adsorption and Na and K were measured by flame emission. Carbonate, HCO_3 and Cl concentrations were titrated with H_2SO_4 and $AgNO_3$ (USDA, 1954, p. 145–146). Sulfate concentrations were measured turbidimetrically on a spectrophotometer (Tabatabai and Bremner, 1970). Electrical conductivity and pH were also measured. All sample containers and extracting equipment were plastic to avoid fluoride-glass interactions.

Fluoride and calcium activities were calculated and from these data, the fluoride ion activity product $[(Ca) (F)^2]$ was calculated for each sample. This was done by first calculating the ionic strength (Griffin and Jurinak, 1973) and then the mono- and divalent activity coefficients using the Davies equation (Stumm and Morgan, 1970, p. 83) as:

$$-\log\gamma_z = .509(Z)^2 (1^{1/2} /(1 + 1^{1/2}) - 0.31)$$

where γ_z is the activity coefficient for ions with charge Z in a solution with ionic strength 1. Since these soils are calcareous with pH values greater than 8.0 the ion pairs $CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$, $CaSO_4^0$, CaF^+, $MgCO_3^0$, $MgHCO_3^+$, $MgOH^+$, $MgSO_4^0$, MgF^+, $NaSO_4^-$, and $NaCO_3^-$ were considered significant and were accounted for (Robbins et al., 1980). Boron-fluoride pairs were ignored because of very low measured soil and water B concentrations and Fe and Al solubility above pH 8 was assumed to be low enough that their ion pairing with F would be insignificant. Preliminary studies on these soils with phosphate and the experience of others (Nordstrom and Jenne, 1977) suggest that phosphate-fluorite ion pairing can also be ignored in calcar-

[3] The use of brand names are for the reader's convenience and do not imply endorsement of these brands over any other by the authors or the sponsoring institutions.
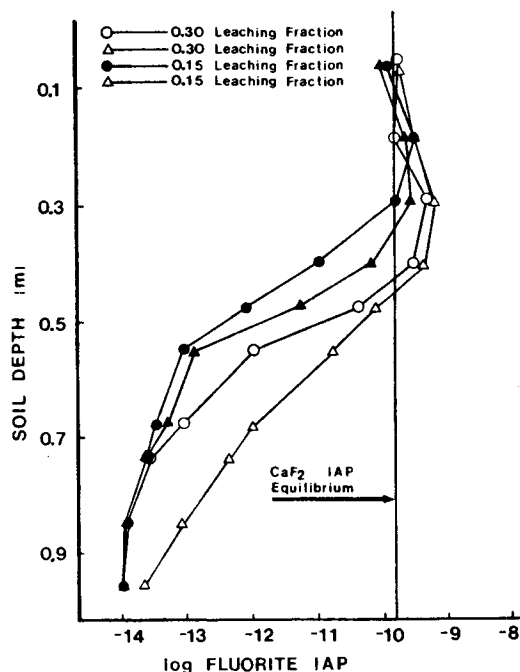

Fig. 1—Log fluorite ion activity product (IAP) values in 2:1 soil/water extracts with depth in lysimeter study.

eous soils. The ion pair stability constants were all taken from Adams (1971), except the MgF^+ and CaF^+ stability products (Nordstrom and Jenne, 1977).

The fluorite ion activity products were calculated on the 2:1 soil/water extracts and those soil samples that appeared to contain fluorite due to the extracting solutions being saturated with respect to fluorite (Fig. 1) were again extracted with 1:1, 1:2, or 1:4 soil/water extracts in order to dissolve the precipitated fluorite (CaF_2) as indicated by the log IAP being < -9.77. Fluorite X-ray diffraction identification was not used because detection of F at low levels was not possible. Cation and anion concentrations and pH and EC were also measured on these extracts.

RESULTS AND DISCUSSION

Less than 2% of the applied F was measured in the leachate from any lysimeter. After the initial leachate sample, the F concentration in the leachate remained below 0.75 mg/L (Fig. 2) and the leachate CaF_2 log IAP was always below -11 (Fig. 3). The maximum legal F concentration in drinking water for southern Idaho is 2.0 mg F/L.
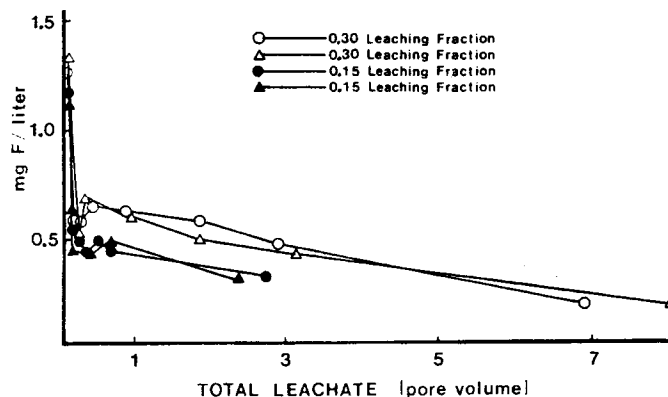
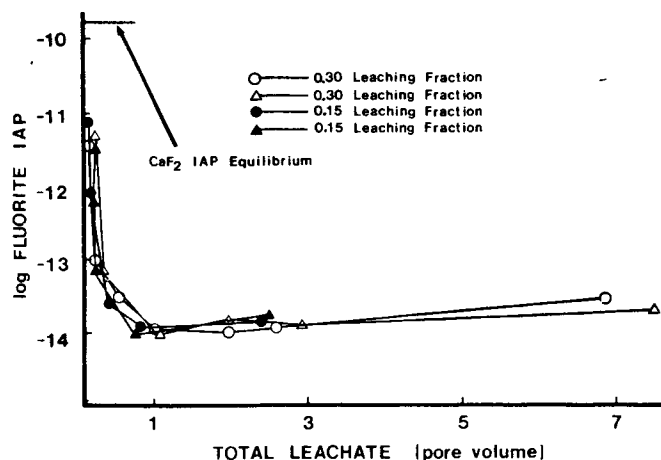

Fig. 2—Fluoride concentration in lysimeter leachate.

Fig. 3—Log fluorite ion activity product (IAP) in lysimeter leachate.

The F concentration in the 2:1 soil/water extracts (Fig. 4) indicate fluoride was being concentrated in the upper portion of the soil columns, but as time progressed from 330 d (not shown) to 600 d and as more water and F was applied with the 0.30 leaching farction than with the 0.15 leaching fraction, the high F concentrations moved to lower points in the profile.

The ion activity product for fluorite [IAP = (Ca) $(F)^2$] from these samples (Fig. 1) suggest that the upper part of the profile was saturated with respect to fluorite if we use the log IAP suggested by Roberson and Shoen (1973) of -9.77. We used -9.77 as equilibrium because our data consistently gave a larger log IAP value than -10.96 as suggested by Nordstrom and Jenne (1977), or -10.41 (Lindsay, 1979).

Those samples which appeared to contain fluorite were extracted with increasingly larger volumes of water until the log IAP dropped below -9.77. These dilutions and F concentrations were used to calculate the water-soluble F, which from the log IAP appeared to be fluorite (CaF_2). This is shown in Table 2 as the soluble F. The unmeasured or unrecovered F is assumed to be absorbed by the soil minerals or precipitated as a less soluble mineral. Phosphate additions to these samples in the 1 to 10 mmol range and shaken overnight did not appear to affect the F solubility under these conditions. It is assumed that fluorapatite formation was too slow to be measured.

From these data it was concluded that more than one mechanism was involved in F removal from soil solution. Between 75 and 85% of the added fluoride was adsorbed or precipitated by a mechanism that kept the F activity below that required for fluorite precipitation. Once this mechanism was saturated, the F activity increased until fluorite precipitation started to take place. Fifteen to twenty-five percent of the added fluoride appeared to be precipitated as fluorite and less than 2% of the applied F was accounted for in the leachate.

Under these conditions the soil could act as a F sink when the combined Ca and F activities exceeded the fluorite ion activity product. The other fluoride removal mechanism appears to have an upper limit as to the amount of F it can remove from soil solution, even though it initially can reduce fluoride concentration to below acceptable drinking water standards.
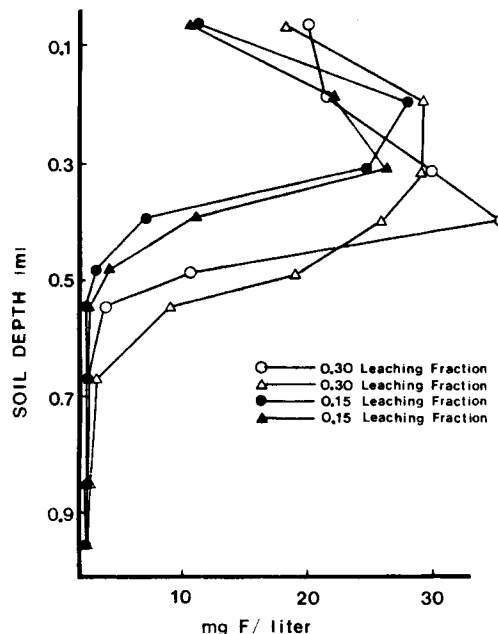

Fig. 4—Fluoride concentration in 2:1 soil/water extracts from lysimeter study.

Fluorite solubility in this soil allowed the F concentrations to get as high as 24 mg F/L in the root zone. These high concentrations could in time have an effect on the F concentrations reaching shallow ground waters. Further studies should include gypsum or $CaCl_2$ applications on F concentrations as affected by Ca activity in the soil solution, and a detailed study of the other mechanism or mechanisms involved in removing F from solution in calcareous soils. Additional laboratory work on phosphorus-fluoride interactions is currently under way.

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